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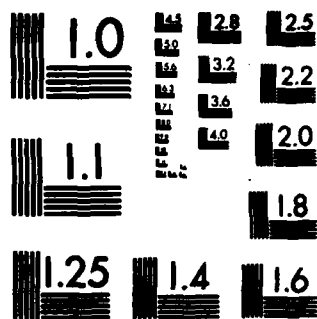UNCLASSIFIED   N00014-80-C-0779   F/G 11/9   NL

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Fourier Transform Infrared Study of the

Polymer-Dopant Interaction in Polyacetylene

by

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Research Report

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ABSTRACT: Fourier Transform Infrared (FTIR) measurements of AsF_5 doped $(CH)_x$ with dopant concentrations which vary over three orders of magnitude have been obtained in both the mid (4000-400 cm^{-1}) and far (400-15 cm^{-1}) infrared. The bandwidths of the strong bands characteristic of the doped polymer have been observed to be invariant with dopant concentration. However, the frequency positions of these new IR bands are found to be a sensitive function of the dopant level. In the far infrared, no evidence of the predicted soliton pinning mode was found for any of the dopant concentrations studied. The consequence of these results in view of current theoretical models of the polymer-dopant interaction is discussed.

INTRODUCTION

Considerable interest and controversy has arisen concerning the understanding of the doping mechanism responsible for the high conductivity exhibited by polyacetylene, $(CH)_x$, after treatment with oxidizing or reducing agents.[1,2] Vibrational spectroscopy[3-10] has played an important role in this understanding, but the interpretation of the experimental results has not been straightforward. Initial results[7] in the infrared reported two strong features at 1370 cm^{-1} and 900 cm^{-1} in lightly doped $(CH)_x$, independent of the dopant species; the latter band was initially attributed to an ionization of donor or acceptor states in the doped material. However, FTIR studies on heavily[8] AsF$_5$ doped $(CH)_x$ and $(CD)_x$ soon demonstrated that a number of medium to weak bands were also observable in the IR spectrum in addition to the two strong features previously reported.[7] Furthermore, all bands were observed to undergo isotopic shifts to lower frequency in AsF$_5$ doped $(CD)_x$ and on this basis were assigned to molecular vibrations. A vibronic enhancement mechanism was proposed to explain the origin of these intense IR bands, their large bandwidth and their frequency shifts and intensity changes at low temperature. Subsequent studies on doped $(CH)_x$ and β-carotene supported this interpretation[9,10] but disagreed as to the molecular symmetry assigned to these new IR bands. An alternative explanation based fundamentally on the same electron-phonon coupling mechanism, but specifically involving a soliton-like defect mode, has also been proposed and attempts to explain the observed IR data on this basis have appeared in the literature.[11-15]

It is the purpose of this work to report the results of a spectroscopic study in both the mid and far infrared of AsF$_5$ doped $(CH)_x$ with a dopant concentration which varies over three orders of magnitude.[16] In particular, studies in the low frequency region were initiated in order to determine whether a theoretically-predicted soliton pinning mode[14] was present.

The consequences of these experimental results will be discussed in relation to the current proposed explanations of the infrared spectrum of doped $(CH)_x$.

EXPERIMENTAL

All spectra were obtained with an IBM 90 series evacuated Fourier transform interferometer. The number of scans collected at a resolution of 2 cm^{-1} ranged from 128 for lightly doped $(CH)_x$ in the mid infrared (4000-400 cm^{-1}) to 3000 scans for heavily doped $(CH)_x$ in the far infrared (400-15 cm^{-1}). Band positions were determined by a graphics activated cursor and are accurate to ± 0.2 cm^{-1}.

Polyacetylene films for the light doping experiments were prepared by the procedure of Ito et al.[17] The preparation of the thin films on CsI substrates has been described previously.[8] All samples were predominantly cis before doping. AsF_5 doping was carried out by the procedure of Ikehata et al.[18]

Far infrared spectra of heavily doped $(CH)_x$ were obtained by polymerizing $(CH)_x$ directly on a TPX poly(4-methylpentene-1) window and doping the composite structure with AsF_5. Measurements down to 15 cm^{-1} were obtained using an Infrared Laboratories germanium bolometer operating at 1.7°K. Since the transmission of this heavily doped sample was very low, only low temperature detection produced IR spectra with an acceptable S/N ratio.

RESULTS AND DISCUSSION

A. Infrared Spectra as a Function of Dopant Concentration

In Table I are listed the IR band positions of three AsF_5 doped $(CH)_x$ samples whose dopant concentration varies over three orders of magnitude. It is interesting to note that the observed features in both heavily and lightly doped $(CH)_x$ are strikingly similar and differ only in the amount of shift experienced with increased dopant concentration. As can be seen, the most prominent bands at 1403 and 901 cm^{-1} in the lightly doped sample undergo the largest shift to 1385 and 832 cm^{-1}, respectively, in the most heavily doped material. Other bands experience little or no shift. The nature of this result has interesting implications when considered in light of the proposed models of polymer-dopant interaction.[7-15] Rabolt et al.[8] initially interpreted the IR data in terms of a vibronic intensity enhancement mechanism and suggested that the shift of the two most intense bands at 1385 and 832 cm^{-1} in heavily doped $(CH)_x$ from their corresponding positions ($\sim$1550 cm^{-1} and $\sim$1000 cm^{-1} in the Raman)[19] in pristine $(CH)_x$ could be attributed to weakening of the C-C and C=C force constants due to electron transfer to the dopant molecule. It would then be expected that as the number of dopant molecules which react with the chain increases, i.e., the dopant concentration increases, then the "effective" skeletal stretching force constants would decrease. This would result in a shift of bands to lower frequency and is, in fact, observed. The amount of shift (also applicable to the weaker bands) would depend on the amount of C-C and C=C stretching contribution to the potential energy distribution of each normal mode and would be largest for those modes which approach pure skeletal vibrations ($\sim$1550 and 1000 cm^{-1} Raman bands).[19]

In a recent work, Etemad et al.[15] suggested that in the dilute concentration limit, IR absorption arises from solitons, rather than collective modes of the polymer chain since,

although the band intensities are proportional to the dopant concentration, the frequencies are not. However, as is shown in Fig. 1 and Table I, the bands vary significantly with concentration. In fact, the band at 1385 cm^{-1} in heavily doped $(CH)_x$ appears to show a linear dependence with the logarithm of dopant concentration (see Fig. 1). In light of these new results, the conclusions of Etemad et al.[15] must be reexamined.

B. Bandwidth Considerations in Doped $(CH)_x$ and $(CD)_x$

Earlier studies[8] of AsF_5 doped $(CH)_x$ and $(CD)_x$ indicated that the intense bands at 1385 and 832 cm^{-1} had full widths at half maxima (FWHM) which were in the range of 100 cm^{-1}, much larger than that observed for a totally disordered molecule of polyethylene in the melt. This is shown clearly in Fig. 2. It is interesting to note that, within experimental error, the bandwidth of the 1385 cm^{-1} band (and not as obviously the 800-900 cm^{-1} band) does not change with dopant concentration. This is consistent with our initial interpretation[8] of the origin of these bands which attributed the large bandwidth to a simultaneous activation in the infrared of the skeletal stretching vibrations (C=C and C-C) corresponding to all the various conjugation lengths. As Harada et al.[4] have shown, in the Raman spectrum of pristine $(CH)_x$ the position of the CC stretching mode varies from 1466 to 1595 cm^{-1} depending on the wavelength used for Raman excitation. This was interpreted in terms of a distribution of uninterrupted conjugation lengths from 4-100 double bonds, each of which absorbs in a different region of the visible and hence gives rise to a different resonance Raman peak. After doping the activation of all these modes simultaneously in the IR because of a breakdown in the optical selection rules would give rise to a very broad band profile, essentially a histogram of the various conjugation lengths of doped polymer with a FWHM independent of dopant concentration.

On the other hand, when comparing the bandwidths of corresponding bands in heavily doped $(CH)_x$ and $(CD)_x$, it was found that the 1385 cm^{-1} (832 cm^{-1}) band in AsF$_5$ doped $(CH)_x$ (which shifts to 1088 cm^{-1} (670 cm^{-1}) in AsF$_5$ doped $(CD)_x$) had undergone a 50% increase in FWHM. This observation initially appeared to be inconsistent with the band broadening mechanism described above. However, recent studies[20,21] have established that in pristine $(CD)_x$ the resonance enhanced Raman lines characteristic of the skeletal stretching vibrations extend over a much broader range than those in pristine $(CH)_x$. In fact conjugation lengths of 4-200 double bonds would appear to exist in $(CD)_x$ based on the criterion established for $(CH)_x$. This is somewhat puzzling, but normal coordinate calculations by Schugerl and Kuzmany[21] have provided at least a qualitative insight into this observation. Using a fixed set of valence force constants and a fixed molecular geometry, it was found that upon "deuteration" of $(CH)_x$ the conjugation length dependence of the skeletal stretching modes (C=C and C-C) increased, and hence the resonance Raman excitation profile for these bands extends over a larger region in $(CD)_x$. This arises because there is a greater contribution of C=C stretching to the potential energy distribution of the skeletal stretching vibrations in $(CD)_x$. Thus the isotopic shift of the skeletal stretching mode in $(CH)_x$ was found to be larger for each conjugation length, leading to an effective smearing or broadening of the band profile. Simultaneous activation of all these modes in the IR would then be responsible for the larger bandwidth observed in AsF$_5$ doped $(CD)_x$.

C. Far Infrared Measurements

In one attempt to explain the IR spectrum of lightly doped $(CH)_x$, a model based on electronic defects or solitons was proposed.[13]   A calculation of the normal modes of $(CH)_x$ using five force constants to predict the three observed Raman frequencies at 1020, 1080 and 1474 cm^{-1} was reported.[14] This "force field" included an adjustable parameter to

account for electron-phonon coupling. To calculate the vibrational modes of doped (CH)$_x$ including the proposed charged soliton, a term was also included which coupled charge density fluctuations in the π electron gas through the phonons. In this case two dopant-related modes at 980 and 1360 cm^{-1} were calculated and found to agree with those observed at 900 and 1380 cm^{-1} by Fincher et al.[7] No attempt was made to explain the origin of the five additional medium to weak bands which appear in the 1500-500 cm^{-1} region. In addition, the positioning of the narrow (~25 cm^{-1}) calculated bands inside the exceptionally broad (120-150 cm^{-1}) observed band profiles is hardly an acceptable criterion for a "good fit". The numerical agreement with the two strong bands observed experimentally may be fortuitous since the applicability of such an underdetermined force field is, at best, suspect. A conventional force field refinement[22] (22 force consstants, 110 frequencies) requires significantly more frequencies than force constants.

In addition, a third mode characteristic of a charged soliton bound to an ionized dopant site was predicted by calculations[14] based on a continuum model. This new mode characteristic of the soliton-dopant interaction was expected to lie in the 300-500 cm^{-1} region. In Fig. 3 is shown the far infrared spectrum of pristine and AsF$_5$ doped (CH)$_x$ in the 500-200 cm^{-1} region. The strong band at 455 cm^{-1} is characteristic of the cis isomer[23] and the weak band observed at 396 cm^{-1} in the lightly doped material has been attributed[6] to the AsF$_6^-$ anion. The slight increase in absorption observed near 200 cm^{-1} in Fig. 3 arises from the CsI windows used to prevent exposure of the sample to air. The IR spectrum in the 120-15 cm^{-1} region of pristine, lightly doped and heavily doped (CH)$_x$ is shown in Fig. 4. Again no bands are observed in this region or in the 200-120 cm^{-1} region (not shown) which might be assigned[14] to a soliton pinning mode. The heavily doped material shows an overall increase in absorption throughout the infrared as expected for a material exhibiting

metallic-like conductivity. Hoffman *et al.*[24] have recently observed a broad absorption in the far infrared in lightly I_2 doped $(CH)_x$, but concluded that it was too weak to be the soliton pinning mode. No such feature was observed in our work on AsF_5 doped $(CH)_x$, which may suggest that it is attributable to the vibrations of I_3^- or I_5^-, since Raman bands of these anions have been observed in this region.[3] The apparent absence of any soliton pinning mode in the IR has recently led to a reexamination[25] of the soliton predictions and it has been suggested that interactions between the pinned soliton and acoustic phonons might cause a reduction in oscillator strength or possibly shift this mode to higher frequency where it would be obscured by the broad intense bands characteristic of the doped polymer.

CONCLUSIONS

Infrared spectra of AsF_5 doped $(CH)_x$ with dopant concentrations ranging over three orders of magnitude have been obtained in both the mid and far infrared regions. The general features of both lightly and heavily doped $(CH)_x$ are very similar with a total of eight new bands attributable to the doped polymer. These new absorptions shift as a function of dopant concentration with the dominant bands at 1403 and 901 cm^{-1} in lightly doped $(CH)_x$ exhibiting the largest shift. Overall, however, the spectra of lightly and heavily doped $(CH)_x$ are remarkably similar. Since the soliton model should not be applicable at heavy doping levels, it is difficult to understand this striking similarity in terms of the soliton mechanism. In addition, no evidence of a soliton pinning mode in the far infrared has been found for any dopant concentration. The presence of such a mode had been predicted by a continuum model calculation of the soliton. Moreover, it should be noted that the activation and intensity enhancement of skeletal stretching modes in the IR appears to be a general observation even in conducting polymers without degenerate ground states, as evidenced by recent studies ⌐ ˙vpy˙ ⌐.[26] In this system current soliton models cannot be applied.

In general, the understanding of the doping mechanism in polyacetylene has progressed considerably since initial structural measurements were reported. Much new information has appeared and the current theoretical models must now be reexamined and appropriately refined in light of these new data.

ACKNOWLEDGMENTS

TABLE I

Infrared Band Positions (cm^{-1}) in AsF_5 Doped $(CH)_x$

Dopant Concentration

0.03%	0.1%	10%
1403	1401	1385
1295	1290	1290
1177	1177	1180
901	898	832
817	814	---

REFERENCES

1. T. C. Clarke and G. B. Street, *Synth. Metals* 1, 119 (1980).

2. A. G. MacDiarmid and A. J. Heeger, *Synth. Metals* 1, 101 (1980).

3. S. L. Hsu, A. J. Signorelli, G. P. Pez and R. H. Baughman, *J. Chem. Phys.* 69, 106 (1978).

4. I. Harada, M. Tasumi, H. Shirakawa and S. Ikeda, *Chem. Lett.* 1411 (1978); H. Shirakawa, T. Sasaki and S. Ikeda, *Chem. Lett.* 1113 (1978).

5. S. Lefrant, L. S. Lichtmann, H. Temkin and D. B. Fitchen, *Solid State Comm.* 29, 191 (1979).

6. T. C. Clarke, R. H. Geiss, W. D. Gill, P. M. Grant, J. W. Macklin, H. Morawitz, J. F. Rabolt, D. Sayers and G. B. Street, *J. Chem. Soc., Chem. Comm.* 7, 332 (1979).

7. C. R. Fincher, M. Ozaki, A. J. Heeger and A. G. McDiarmid, *Phys. Rev. B* 19, 4140 (1979).

8. J. F. Rabolt, T. C. Clarke and G. B. Street, *J. Chem. Phys.* 71, 4614 (1979).

9. I. Harada, Y. Furukawa, M. Tasumi, H. Shirakawa, S. Ikeda, *J. Chem. Phys.* 73, 4746 (1980).

10. I. Harada, Y. Furukawa, M. Tasumi, H. Shirakawa and S. Ikeda, *Chem. Lett.* 267 (1980).

11. M. J. Rice, *Phys. Lett.* 71A, 152 (1979).

12. W. P. Su, J. R. Schrieffer and A. J. Heeger, *Phys. Rev. Lett.* 42, 1698 (1979).

13. M. J. Rice and E. J. Mele, *Solid State Comm.* 35, 487 (1980).

14. E. J. Mele and M. J. Rice, *Phys. Rev. Lett* 45, 926 (1980).

15. S. Etemad, A. Pron, A. J. Heeger, A. G. MacDiarmid, E. J. Mele and M. J. Rice, *Phys. Rev. B* 23, 5137 (1981).

16. J. F. Rabolt, T. C. Clarke and G. B. Street, International Conference on Low Dimensional Conductors, Boulder, Colorado, August, 1981.

17. T. Ito, H. Shirakawa and S. Ikeda, *J. Polym. Sci. A1* 12, 11 (1974).

18. S. Ikehata, J. Kaufer, T. Woerner, A. Pron, M. A. Druy, A. Sivak, A. J. Heeger and A. G. MacDiarmid, *Phys. Rev. Lett.* 45, 1123 (1980).

19. H. Shirakawa, T. Ito and S. Ikeda, *Polymer J.* 4, 460 (1973).

20. L. Lichtmann, S. Sarhangi and D. Fitchen, *Solid State Comm.* 36, 869 (1980).

21. F. B. Schugerl and H. Kuzmany, *J. Chem. Phys.* 74, 953 (1981).

22. J. F. Rabolt, W. H. Moore and S. Krimm, *Macromolecules* 10, 1065 (1977).

23. H. Shirakawa and S. Ikeda, *Polymer J.* 2, 231 (1971).

24. D. M. Hoffman, D. B. Tanner, A. J. Epstein and H. W. Gibson, *Mol. Cryst. Liq. Cryst.* (to be published).

25. E. J. Mele, International Conference on Low-Dimensional Conductors, Boulder, Colorado, August, 1981.

26. G. B. Street, T. C. Clarke, M. Krounbi, K. Kanazawa, V. Lee, P. Pfluger, J. C. Scott, G. Weiser, *Molecular Crystals and Liquid Crystals* (to be published).
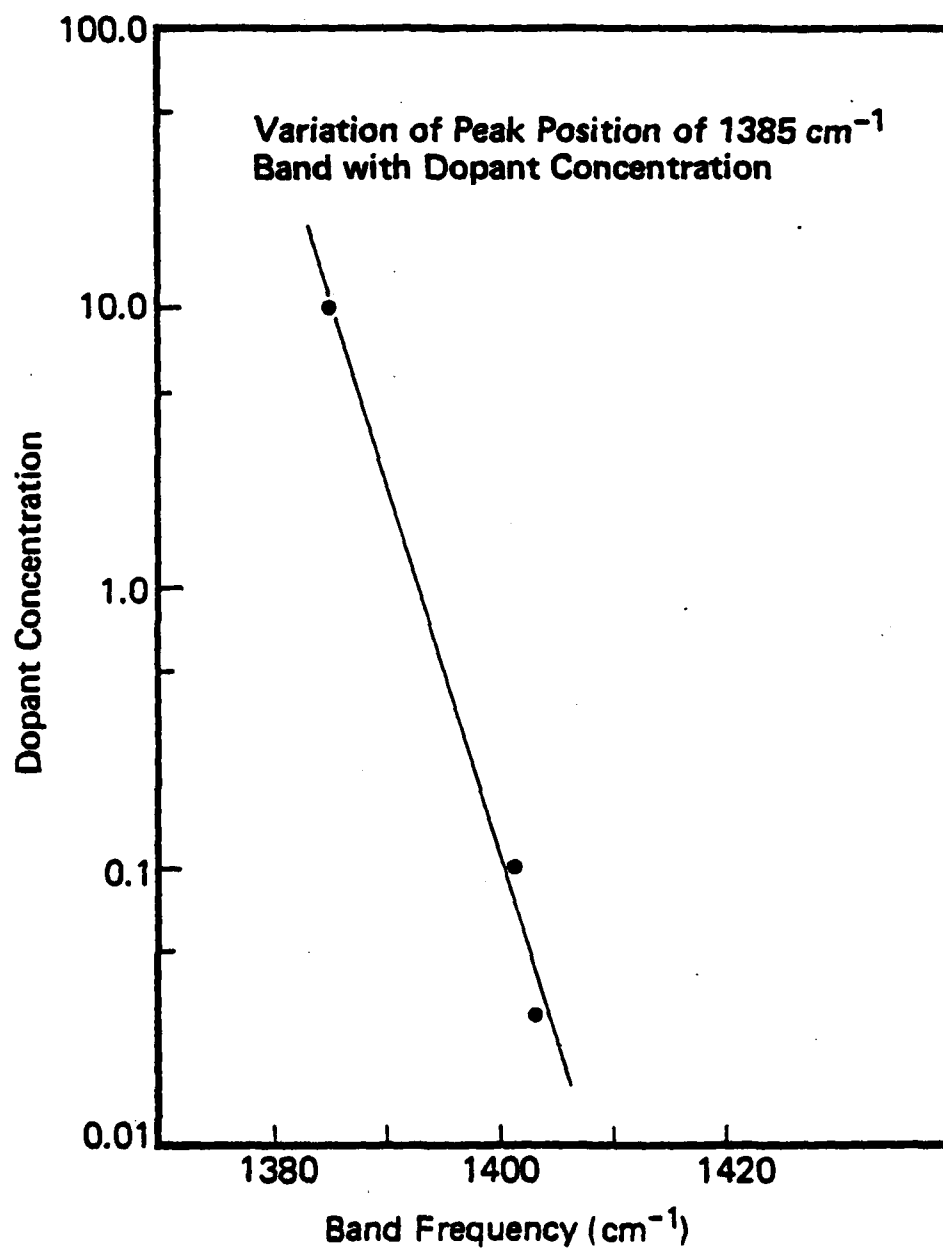
Figure 1. Plot of the frequency position of the 1385 cm^{-1} band in AsF$_5$ doped (CH)$_x$ versus the logarithm of the dopant concentration.
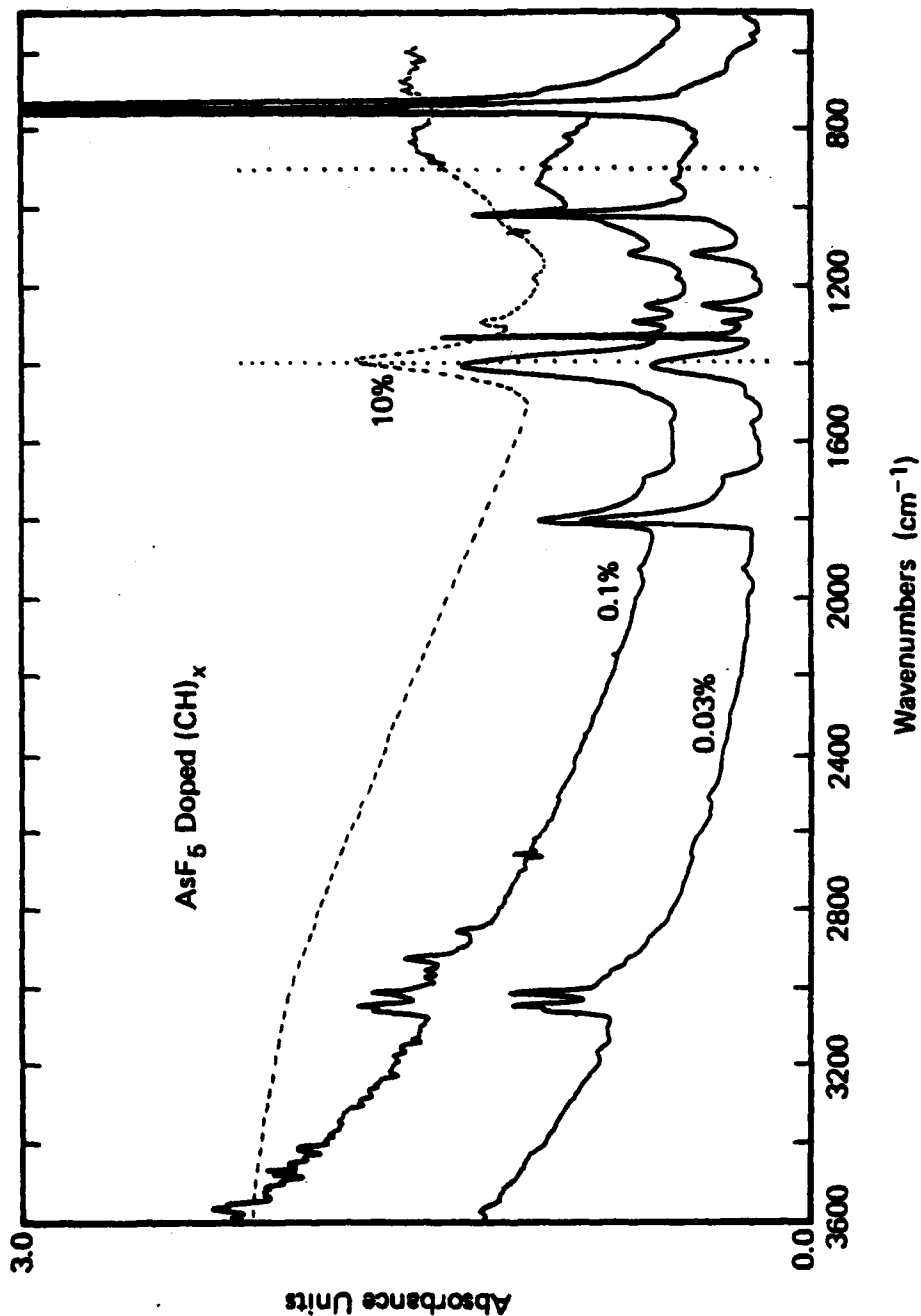
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Figure 2. Infrared spectra (3600-500 cm^{-1}) of AsF$_5$ doped (CH)$_x$ at dopant concentrations of 0.03, 0.1 and 10%. Heavily doped (10%) spectrum is on a different Absorbance scale since a much thinner film had to be used. If put on the same scale, the absorptions of such a "metallic" material would be off scale in this region.
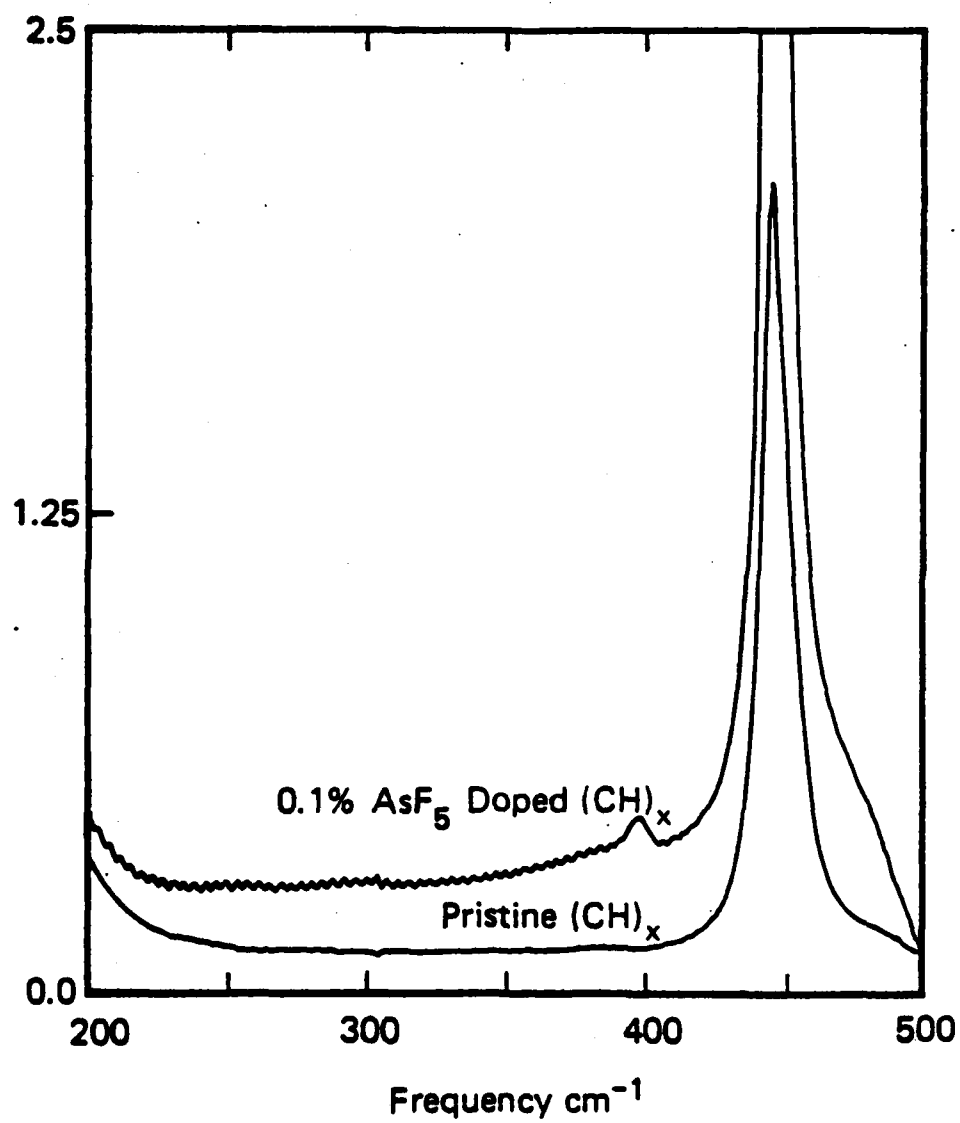
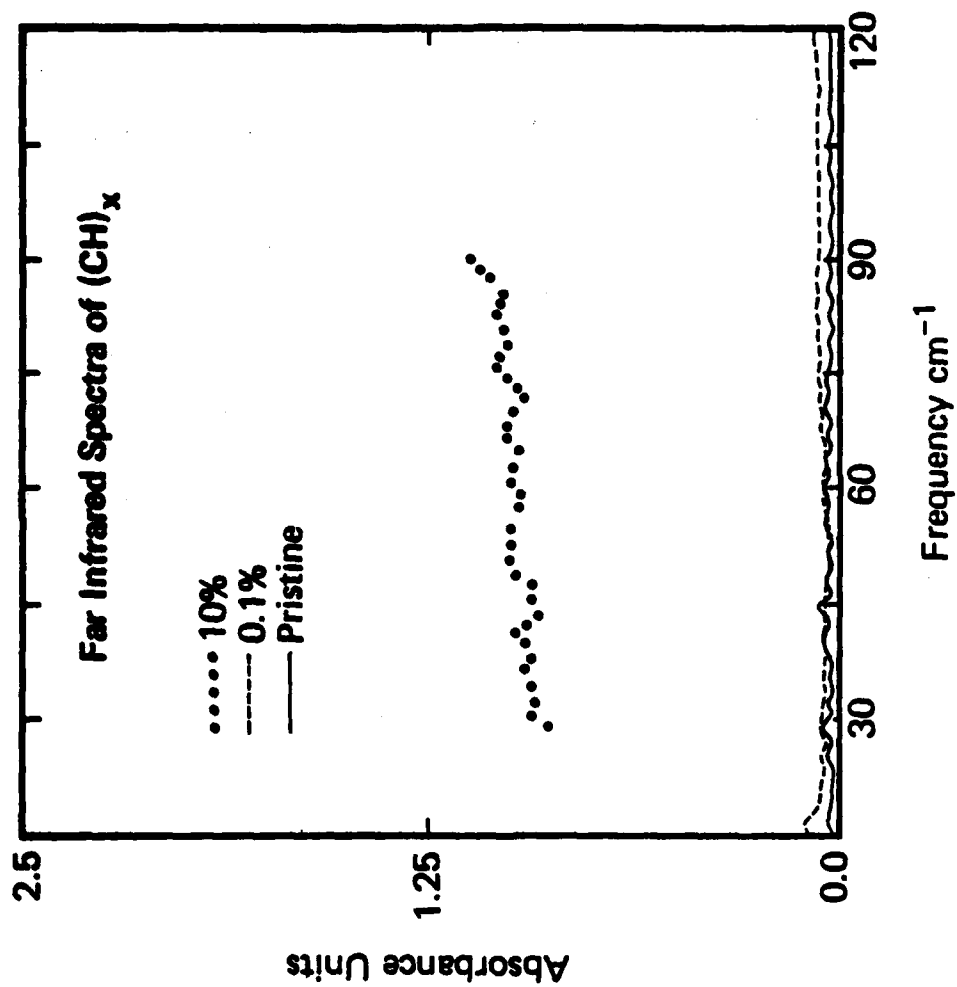Figure 3. Far infrared spectra (500-200 cm⁻¹) of intermediately AsF₅ doped and pristine (CH)ₓ.

Figure 4. Low frequency infrared spectra (120–15 cm⁻¹) of pristine, intermediately (0.1%) doped and heavily doped (CH)ₓ.